GALVANIZED ALUMINIUM SHEET

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Abstract of WO9743467

In a method for applying a zinc layer onto an aluminium or aluminium alloy sheet, comprising pretreating the surface and applying the layer by electrolytic galvanizing, the pretreating comprises electrochemical graining of said surface, for example in a solution having a pH less than 3 with an alternating current applied between the sheet and an electrode. In an alternative method, the pretreating includes applying a preliminary zinc layer by immersing the surface in a zinc-containing alkaline solution, applying a potential to the sheet and reversing the polarity of said potential at least once. The sheets are useful as for example building cladding sheets and automotive panels.

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(57) Abstract

In a method for applying a zinc layer onto an aluminium or aluminium alloy sheet, comprising pretreating the surface and applying the layer by electrolytic galvanizing, the pretreating comprises electrochemical graining of said surface, for example in a solution having a pH less than 3 with an alternating current applied between the sheet and an electrode. In an alternative method, the pretreating includes applying a preliminary zinc layer by immersing the surface in a zinc-containing alkaline solution, applying a potential to the sheet and reversing the polarity of said potential at least once. The sheets are useful as for example building cladding sheets and automotive panels.

GALVANIZED ALUMINIUM SHEET

TECHNICAL FIELD

The invention relates to methods for applying a
layer comprising zinc onto at least one surface of an
aluminium or aluminium alloy sheet, comprising in
succession a pretreatment step and an electrolytic
galvanizing step. The invention also relates to the
galvanized aluminium or aluminium alloy sheet produced by
the methods, and the use of such sheet in building
structures and as automotive body sheet. In the
following description, for brevity we refer to aluminium
sheets, but this term is to be understood to include
aluminium alloy sheets.

BACKGROUND ART

Aluminium sheet is used on a wide scale in
building structures as interior and/or exterior panels of
buildings both for façade and roofing structures. An
advantage of this is that the low specific weight of the
aluminium means that the building structure may be made
considerably lighter than for example with steel sheet.
A disadvantage of untreated aluminium sheet is that the
building structure reflects a large amount of light which
limits its application in the immediate vicinity of
airfields, for example. A solution to this problem is to
provide the aluminium sheet with a surface layer, for
example zinc, while retaining the structural advantages.
An advantage of a galvanized aluminium sheet is that it
reflects less light and has good corrosion resistance. A

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further advantage of galvanized aluminium sheet is that

the building structure made with it requires little

maintenance due to the durability of the AlZn system. A

further advantage of galvanized aluminium sheet is that

5   the appearance of the aluminium sheet changes slowly over

time, i.e. it "lives". This last property, the so-called

patina effect, is much sought after by architects for

application in buildings of their design. Galvanizing

the aluminium sheet considerably increases the

10   applicability of the aluminium sheet.

Methods of electrolytically plating zinc onto

aluminium (galvanizing) are well known. To improve the

applied zinc layer, pretreatments of the aluminium

surface have been proposed.

15   JP-A-52005630 discloses electroplating one of Cu,

Ni, Zn, Sn, Pb, Cd and Cr onto the chemically roughened

surface of an aluminium or aluminium workpiece. The

roughening is performed in two stages: first in alkali

pH $\geq$ 11 or a fluoric acid solution, and second using a

20   mixed mineral acid solution.

In EP-A-0497302 a pretreatment step consisting of

degreasing and pickling is performed and cathodic zinc

electroplating is then carried out in two steps, thereby

forming two adjacent zinc layers. The layers may contain

25   Ni or Fe additions to improve bonding.

Another method for pretreating and galvanizing an

aluminium sheet is given in EP-A-0498436, which describes

a method for the continuous electrolytic application of a

zinc layer onto an aluminium sheet intended for

processing into an automotive body sheet, after which the

aluminium sheet is provided with a paint layer. The

method comprises in succession the steps (i) alkaline

degreasing, (ii) pickling in an acid solution, (iii)

anodizing and cathodic zinc electrolysis of the aluminium

sheet in the same acid solution. In between the steps

the aluminium sheet is cleaned by rinsing with water.

The anodization and electrolysis process is not dependent

on the extent of pretreatment, which may even be omitted.

A disadvantage of galvanized aluminium sheet obtained by

this method is that the bonding of the applied zinc layer

on the aluminium sheet is very poor when the galvanized

aluminium sheet is highly deformed, for example by

bending.

Zinc plating of wrought aluminium sheet as a

precursor to zinc phosphate treatment and painting is

described in US-A-5176963. The zinc plating may comprise

two stages, namely displacement plating from an alkaline

bath and electroplating from an acid bath. There is no

disclosure of the application of a potential to the sheet

during the displacement plating stage.

DISCLOSURE OF THE INVENTION

An object of the invention is to provide a method

for pretreating and galvanizing an aluminium sheet by

which a very effective bond is obtained between the

applied zinc layer and the aluminium sheet, the bond

remaining effective under large subsequent deformation of

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the sheet. An additional object of the invention is that the method for pretreating and galvanizing the aluminium sheet may be carried out as a continuous process.

According to the invention in one aspect there is provided a method for applying a layer comprising zinc onto at least one surface of an aluminium or aluminium alloy sheet, comprising the steps of pretreating said surface and applying the layer by electrolytic galvanizing, characterized in that the pretreating step comprises electrochemical graining of said surface.

Electrolytic graining is a process known in the art and is one example of the technique of graining. It is known in the art (see "Study of the mechanism of the A.C. electrolytic graining of aluminium" by P. Laevers, Brussels Free University, November 1995 and EP-A-586504) to use electrolytic graining for roughening of aluminium sheet, typically an aluminium-litho sheet, but the use of graining as a pretreatment in electrolytic galvanizing of aluminium sheet is novel.

By the electrochemical graining pretreatment step of the invention an effective bond between the electrolytically applied zinc layer and the aluminium sheet is formed, the bond remaining effective during subsequent deformation of the aluminium sheet, for example by bending. It can also achieve the effect that the resulting aluminium sheet has a very good corrosion resistance. Furthermore the method may be carried out in a continuous process.

The invention is based in part on the insight that to obtain a well-bonded zinc layer on the aluminium sheet so that the bond remains effective under great deformation of the galvanized aluminium sheet, the pretreatment is extremely important. It is believed that the electrochemical graining of the aluminium sheet produces a roughened surface so that the subsequently electrolytically applied zinc layer is also mechanically bonded. This mechanical bonding is partly responsible for achieving the effect that the zinc layer remains bonded under large deformation of the galvanized aluminium sheet.

Very good results, including effective bonding of the electrolytically applied zinc layer may be obtained with graining process parameters comprising one or more of:

(a) alternating current, preferably with a frequency in the range from 10-1000 Hz, more preferably 40-100 Hz;

(b) current density of 5-200 A/dm², preferably 10-100 A/dm², and more preferably 20-50 A/dm²;

(c) bath temperature 15-60°C, preferably 40-50°C;

(d) treatment time 0.2-60 s, preferably 0.5-10 s, and more preferably 2-3 s;

(e) bath acidity pH < 3, and preferably pH < 2.

A further advantage is that these process parameters lend themselves to application in a continuous process operation.

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As mentioned, the electrolytic graining is preferably performed in an acid solution. Various acids may be used for this, but preferably use is made of a hydrochloric acid solution or a nitric acid solution. The graining step may be a part of a pretreatment cycle. A typical preferred pretreatment cycle comprises in succession:

(1)   alkaline degreasing;

(2)   electrolyte graining;

(3)   anodizing e.g. in a sulphate solution;

and may also comprise rinsing with water between these steps. However, the method is not limited to this pretreatment cycle. Better alkaline degreasing is achieved if simultaneously a direct current is applied in a range 1-20 A/dm^2, preferably 5-15 A/dm^2.

Preferably anodizing is carried out after the electrolytic graining.

In a further aspect, the invention consists in an aluminium or aluminium alloy sheet having an electrolytically applied layer comprising zinc in which said layer is adjacent to an aluminium or aluminium alloy surface roughened by electrochemical graining. By microscopic inspection of the aluminium-zinc interface it will be possible to detect the electrolytic graining.

In a second method, the invention provides a method for applying a layer comprising zinc onto at least one surface of an aluminium or aluminium alloy sheet, comprising the steps of pretreating said surface and

applying said layer by electrolytic galvanizing, said
pretreating step including applying a preliminary layer
comprising zinc onto said surface, characterized in that
the application of said preliminary layer comprises (i)

5   immersing said surface in a zinc-containing alkaline
solution, (ii) applying a potential to the sheet to cause
an electrolytic current to flow, and (iii) reversing the
polarity of said potential at least once. This method
may be combined with the electrolytic graining

10   pretreatment described above.

By this method of applying a preliminary zinc
layer, a very effective bond of the subsequent
electrolytically applied zinc layer may thereby be
obtained. An advantage of this pretreatment is that the

15   whole pretreatment may be carried out in an alkaline
solution. Thus only a single waste flow, which is
alkaline, may be formed which represents a logistical
advantage. In addition the aluminium sheet can be
directly degreased. The entire pretreatment cycle can

20   therefore consist essentially of one pretreatment step.

Zincate treatments are known for applying
conversion layers onto aluminium, for example as known
from "Oppervlaktebehandelingen van aluminium" by T. van
der Klis and J.W. du Mortier published by the Vereniging

25   voor Oppervlaktetechnieken voor Materialen, Bilthoven,
NL, 3rd edition 1992, pp 406-409. A basic composition
for a zincate pickle comprises 40-50 g/l ZnO and 400-500
g/l NaOH. However, a zincate treatment according to the

present method, besides applying a thin zinc layer onto
the aluminium sheet, also activates the surface of the
aluminium sheet so that the zinc layer applied
electrolytically subsequently bonds better.   The
thickness of the layer comprising zinc produced in the
pretreatment step is not of major importance, but may be
in the range 0.1 to 0.5 g/m^2, and the ultimate layer
thickness of the zinc is essentially determined during
the electrolytic galvanizing stage.

In this second method of the invention, the
aluminium sheet may be anodized, e.g. in a sulphate
solution, prior to the electrolytic galvanizing. This
can achieve the effect that the electrolytically applied
zinc layer bonds very effectively to the aluminium sheet.

In the second method of the invention, during the
zincate treatment, the aluminium sheet changes polarity
at least once, preferably at least twice. Thus the
aluminium sheet may be initially anode-connected (A) for
a given time, and then cathode-connected (C). This
connection sequence may be designated A-C. The aluminium
sheet is preferably anode-connected first so that a part
of the oxide layer goes into solution, after which a thin
zinc layer deposits onto the aluminium sheet at the time
when the aluminium sheet is cathode-connected. However
C-A connection is also possible. The final connection is
preferably as a cathode. Preferably the aluminium sheet
is connected at least A-C-A-C. The duration of
maintenance of each polarity is here called the

electrolysis time per polarity, and is preferably at
least 0.5 s.

Very good results may be obtained with zincate
process parameters comprising one or more of:

(a)   bath temperature 10-60°C, preferably 20-30°C;

(b)   current density of 0.5-20 A/dm^2, preferably 2-10
       A/dm^2;

(c)   electrolysis time per polarity 0.5-10 s,
       preferably 1-4 s;

(d)   total immersion time 1-30 s, preferably 2-10 s;

(e)   bath composition comprising 10-300 g/l NaOH and 2-
       40 g/l ZnO, preferably 50-150 g/l NaOH and 5-20
       g/l ZnO.

An advantage of these process parameters is that the
pretreatment process lends itself well to application in
a continuous process operation.

Following the pretreatment according to both
methods of the invention the aluminium sheet is
electrolytically galvanized in an acid solution.
Conventional galvanizing techniques may be used, and many
different processes are suitable. Good results may be
obtained when the galvanizing process parameters comprise
one or more of:

(a)   direct current with a current density of 10-100
       A/dm^2, preferably 30-70 A/dm^2;

(b)   bath temperature 20-70°C, preferably 40-60°C;

(c)   treatment time 5-90 s, preferably 10-40 s;

(d)   electrolyte composition comprising zinc sulphate
         with 30-200 g/l zinc, preferably 60-120 g/l;

(e)   acidity of the electrolyte pH < 4, preferably
         approximately pH 2.5.

Using these parameters, a well-bonded layer comprising
essentially zinc may be applied to the pretreated
aluminium sheet, the bonding remaining effective under a
large deformation of the galvanized aluminium sheet. A
further advantage is that it is possible to perform a
continuous process. With a pH of approximately 2.5 it is
possible to buffer the electrolyte, thereby making the
electrolytic galvanizing process considerably more
stable.

The electrolyte composition used is not limited to
a composition comprising a sulphate solution, and for
example a chloride solution may also be applied.

According to a preferred version of the first
method of the invention, wherein the pretreatment
comprises electrolytic graining followed by a brief
anodization after which the aluminium sheet is
electrolytically galvanized, desirably the same
electrolyte liquid bath is not used for the anodizing as
for the galvanizing. Working with a continuous process
operation, but one in which the electrolytes for the
anodizing and the galvanizing are separate, has the
advantage that the two process conditions may be
controlled independently. Thus for the anodizing process
preferably a pH < 2 is used, and for the electrolytic

galvanizing preferably a pH of approximately 2.5.
Moreover, the electrolyte for the anodizing may comprise
either zinc sulphate or an iron sulphate, and also such
metals as Ni or Cu, while the electrolyte for the
galvanizing is preferably zinc sulphate.

Both methods in accordance with the invention are
preferably carried out in a continuous process, although
it is possible to carry them out batchwise.

As mentioned, the methods in accordance with the
invention are suitable for galvanizing aluminium sheets
made of aluminium and a wide range of aluminium alloys,
such as aluminium alloys of the 1xxx type, the 3xxx type,
and the 6xxx type, but also of the 2xxx type and the 5xxx
type (AA designations).

The zinc layer applied in the methods of the
invention may be essentially a pure zinc layer or may be
primarily zinc but including minor amounts of impurity
elements or deliberately added elements, as is known in
the art. Typically such impurity elements or added
elements are present at less than 10%, more usually less
than 5% by weight in the zinc layer.

Another advantage of the methods in accordance
with the invention is that the galvanized aluminium sheet
which is produced has an atmospheric corrosion resistance
almost comparable to that of zinc sheet, which has been
used for application in building structures. This
enables structures to be made lighter while retaining the
good corrosion resistance. Moreover, the total zinc

consumption when using galvanized aluminium sheet in

building structures is considerably less than when using

zinc sheets.

The invention also consists in the galvanized

aluminium sheet produced by the methods according to the

invention.

In a further aspect galvanized aluminium sheet,

obtained by either method, may be used in building

systems such as facade and roofing structures, and

windowsill structures. Galvanized aluminium sheet

suitable for application in building systems such as

those known under the trade names KAL-ZIP and KAL-BAU may

be obtained by the invention. In the case of application

of the galvanized aluminium sheet in building structures,

the aluminium sheet preferably comprises a weight per

unit area of applied zinc in the range of 10-300 g/m^2, and

more preferably 30-100 g/m^2.

In another aspect galvanized aluminium sheet,

obtained by either method, may be used in shaping

applications such as for the manufacture of automotive

body parts by pressing. In the case of use of the

galvanized aluminium sheet as automotive body sheet, the

aluminium sheet preferably comprises a weight per unit

area of applied zinc in the range 5-100 g/m^2, and more

preferably in the range 5-40 g/m^2.

BEST MODES OF CARRYING OUT THE INVENTION

The invention will now be illustrated by several

non-limitative examples.

Example 1

Aluminium sheets manufactured from an AA3004 alloy
suitable for application in building structures were
pretreated and electrolytically galvanized in different
ways in batch processes. The bonding of the applied zinc
layer was then tested by the so-called tape method. This
is a rapid method for testing bonding. A piece of tape
or self-adhesive tape, for example such as that used in
offices, is stuck onto the galvanized aluminium sheet and
then pulled off again by hand. A value assessment is
then given to the bondability by allocating a number
where: (1) = excellent, (2) = good, (3) = fair, (4) =
poor, (5) = very poor. For value assessments (1) and (2)
the bonding was also tested using the known zero bending
test and the known lock-form test. For value assessments
(3) to (5) these supplementary bond tests were omitted.
The galvanized aluminium sheets with value assessments of
(1) or (2) were also tested for durability in a
corrosive, maritime industrial environment.

Table 1 gives the main process parameters used and
the value assessment for the bond. Between the different
steps of the pretreatment and the galvanizing the
aluminium sheets were rinsed with distilled water for at
least 5 s.

The degreasing in tests (1) to (14) was carried
out using Percy 6340-29 (trade name) produced by Henkel
Metall Chemicals, concentration 10 g/l, treatment time 3

s, bath temperature approximately 65°C, direct current with a current density of approximately 10 A/dm^2.

The pickling in tests (1), (2), (9), (11) and (12) was carried out in an HCl environment (8% HCl solution), pH = 1, treatment time approximately 5 s. In tests (6) and (7) an 8% H$_2$SO$_4$ solution was used and a treatment time of approximately 5 s.

The graining in tests (3) to (5) was carried out in 1% HCl solution having a pH of about 1, bath temperature approximately 40°C, alternating current of approximately 50 Hz, current density of approximately 50 A/dm^2 and variable treatment time.

The anodizing in tests (5), (7) to (9), (12) and (16) was carried out with direct current, current density approximately 50 A/dm^2, polarity positive, treatment time approximately 5 s, a ZnSO$_4$.H$_2$O electrolyte comprising approximately 90 g/l zinc, pH = 1.8, bath temperature approximately 50°C. In tests (10) and (11) the electrolyte comprised sulphuric acid, other parameters were identical to test (5), except that the temperature was approximately 70°C. In tests (13) and (14) sulphuric acid and phosphoric acid respectively were used for the electrolyte, pH = 1.8, bath temperature approximately 60°C, stainless steel electrode material, alternating current, electrolysis time approximately 2 s, current density approximately 2 A/dm^2, total immersion time approximately 10 s.

In tests (15) to (17) the pretreatment was carried
out by connecting the aluminium sheet A-C-A-C,
electrolysis time per polarity approximately 3 s, bath
temperature approximately 20°C, current density
approximately 5 A/dm², immersion time approximately 10 s,
composition of electrolyte 100 g/l NaOH and 10 g/l ZnO.
The thickness of the zinc layers formed by this zincate
treatment were in the range 0.1 to 0.5 g/m². In test (16)
the aluminium sheet was anodized in addition to that
treatment.

In tests (1) to (16) the aluminium sheets were
electrolytically galvanized in a zinc sulphate
electrolyte with 90 g/l zinc, pH approximately 2, direct
current with a current density of approximately 50 A/dm²,
bath temperature approximately 50°C, immersion time
approximately 20 s. In test (17) the pH was
approximately 2.5, other parameters being identical to
tests (1) to (16). The electrolytically applied zinc
layer was approximately 35 g/m².

It may be inferred from the results given in Table
1 that a pretreatment consisting of degreasing and
pickling (tests 1, 2 and 6) is insufficient to obtain a
well-bonded layer comprising zinc.

A pretreatment consisting of degreasing and
anodizing (tests 8, 10, 13 and 14) is also insufficient
to obtain a well-bonded layer comprising zinc.

The combination of in succession degreasing,
pickling and anodizing (tests 7, 9, 11 and 12) was also

insufficient to obtain a well-bonded layer comprising zinc.

Very good results were obtained when the aluminium sheet was electrolytically grained following the degreasing (tests 3 to 5). The best results were achieved with the method in accordance with test (5), in which anodizing followed the graining.

Very good results were also obtained when the aluminium sheet was pretreated in an alkaline environment comprising zinc while being A-C-A-C connected (tests 15 to 17). Good results were also obtained if, following on from that, an anodization step carried out (test 16).

The galvanized aluminium sheets obtained with the method in accordance with tests (3), (5) and (15) to (17) were also subjected to the zero bending test and the lock-form test. In all cases the bond of the zinc layer and the aluminium sheet remained intact.

Galvanized aluminium sheets manufactured with the method in accordance with tests (3), (5) and (15) to (17) were locally greatly deformed in such a way that the galvanized aluminium sheets were comparable in shape to KAL-ZIP and KAL-BAU. These galvanized aluminium sheets were then tested for durability by means of the Atmospheric Building Corrosion Test as described by B. Boelen in the article "New Product Test: The Atmospheric Building Corrosion Test (ABC Test)", published on the occasion of the ECCA Autumn Congress in Brussels on 27-28 November 1995, and compared with

untreated sheets of AA3004 alloy and pure zinc. After 6
weeks in a maritime industrial surrounding there was no
visible difference between galvanized aluminium and pure
zinc (Reinzink), while the AA3004 alloy was badly

5   corroded particularly by the chloride. Among other
things it can be inferred from the results that
galvanized aluminium sheet manufactured in accordance
with the invention has a durability comparable to a sheet
of pure zinc.

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Table 1

Test	Degreasing		Pickling		Graining		Anodizing		Galvan-izing	Bonding rating
	Temp (°C)	Time (s)	Solution	Temp (°C)	Solution	Time (s)	Solution	Time (s)	pH	
1	65	3	HCl	50	-	-	-	-	2	5
2	65	3	HCl	80	-	-	-	-	2	5
3	65	3	-	-	HCl	30	-	-	2	2
4	65	3	-	-	HCl	5	-	-	2	3
5	65	3	-	-	HCl	3	$ZnSO_4$	5	2	1
6	65	3	H_2SO_4	70	-	-	-	-	2	5
7	65	3	H_2SO_4	70	-	-	$ZnSO_4$	5	2	4
8	65	3	-	-	-	-	$ZnSO_4$	5	2	4
9	65	3	HCl	50	-	-	$ZnSO_4$	5	2	5
10	65	3	-	-	-	-	H_2SO_4	5	2	5
11	65	3	HCl	50	-	-	H_2SO_4	5	2	5
12	65	3	HCl	80	-	-	$ZnSO_4$	5	2	5
13	65	3	-	-	-	-	H_2SO_4	2	2	4
14	65	3	-	-	-	-	H_3PO_4	2	2	4
15	Alkaline solution containing zinc + A-C-A-C connection						-	-	2	1
16							$ZnSO_4$	5	2	1
17							-	-	2.5	1

Example 2

The process as described in test 5 of Example 1 was further performed in eight test runs on a continuous pilot line using AA3004 sheet material 0.26 m wide.

The process parameters used for the eight different test runs are listed in Table 2. In between

graining and anodizing also the sheet was rinsed with

distilled water.

The galvanized sheet which was obtained was tested

for the amount of zinc layer, and the bonding was tested

5   using the zero bending test.

Degreasing was performed in a tank with 10 g/l of

Percy 6340-29 (trade name), with a direct current. After

degreasing, a rinse step was performed. Electrolytic

graining was carried out in 1% HCl solution, with

10   alternating current of 50 Hz. Rinsing with distilled

water followed.

Anodizing was performed in a tank with an

electrolyte having a pH of about 2 comprising 400 g/l

$ZnSO_4 \cdot H_2O$ (resulting in about 90-100 g Zn/l), and 30 g/l

15      $Al_2SO_4 \cdot nH_2O$, and 30 g/l H_3BO_3, and with a direct current.

The H_3BO_3 was added to act as a buffer.

The galvanizing was performed in a separate tank,

but with the same electrolytic composition as used for

anodising. A rinsing step followed.

20   From the results of Table 2 it can be seen that

all the galvanized sheet material had excellent bonding

when tested in a zero bending test. It can also be seen

that the line speed, and hence the treatment time, is an

important process parameter for the amount of zinc

25   coating on the aluminium sheet. At a line speed of 6

m/min (as in Run 5) the contact times for the various

treatment steps were as follows: degreasing 3 s (repeated

four times), graining 5 s, anodizing 5 s, and galvanizing

24 s. The contact times at other line speeds can be

calculated from these values.

Depending on the local conditions a skilled person

can therefore find various optima for the process

parameters depending on the amount of galvanized zinc

required on the aluminium sheet.

Table 2

Run	Line speed (m/min)	Degrease Temp. (°C)	Degrease Current density (A/dm²)	Rinse Temp. (°C)	Graining Temp. (°C)	Graining Current density (A/dm²)	Anodizing Temp. (°C)	Anodizing Current density (A/dm²)	Galvanizing Temp. (°C)	Galvanizing Current density (A/dm²)	Rinse Temp. (°C)	Zinc coating (g/m²)	Bonding rating
1	4	65	15	51	51	29	52	7.7	50	9.6	52	8.0	1
2	12	65	12.8	46	53	29	52	15.3	51	32	52	5.5	1
3	4	65	12.8	43	54	23	51	15.3	51	32	52	14.5	1
4	2	65	12.8	41	57	23	51	7.7	51	32	52	30.5	1
5	6	66	12.8	37	52	19	52	11.5	52	32	53	26.0	1
6	4	66	12.8	41	48	19	51	11.5	54	32	53	25.5	1
7	2	66	12.8	46	45	19	51	7.7	56	32	52	38.0	1
8	4	66	12.8	49	45	38	52	14.2	58	32	52	41.0	1

<u>CLAIMS</u>

1.   A method for applying a layer comprising zinc onto
at least one surface of an aluminium or aluminium alloy
5   sheet, comprising the steps of pretreating said surface
and applying the layer by electrolytic galvanizing,
characterized in that the pretreating step comprises
electrochemical graining of said surface.

10   2.   A method according to claim 1 in which the
pretreating step comprises anodizing said surface after
the electrochemical graining.

3.   A method according to claim 1 or 2 in which the
15   electrochemical graining is performed in a solution
having a pH less than 3 and in which an alternating
current is applied between the sheet and an electrode.

4.   A method according to claim 3 in which the
20   electrochemical graining is performed using a current
density in the range 5 to 200 A/dm^2.

5.   A method according to claim 3 or 4 in which the
alternating current frequency is from 10 to 1000 Hz.

25

6.   A method according to any one of claims 1 to 5 in
which the duration of the electrochemical graining is
from 0.2 to 60 s.

5   7.   A method according to any one of claims 1 to 6 in
which the galvanizing is performed using a direct current
having a current density of from 10 to 100 A/dm^2, a bath
temperature of from 20 to 70°C, a treatment time of from
5 to 90 s, an electrolyte composition comprising zinc

10   sulphate having an amount of zinc from 30 to 200 g/l, and
an electrolyte pH of less than 4.

8.   An aluminium or aluminium alloy sheet having an
electrolytically applied layer comprising zinc in which

15   said layer is adjacent to an aluminium or aluminium alloy
surface roughened by electrochemical graining.

9.   A method for applying a layer comprising zinc onto
at least one surface of an aluminium or aluminium alloy

20   sheet, comprising the steps of pretreating said surface
and applying said layer by electrolytic galvanizing, said
pretreating step including applying a preliminary layer
comprising zinc onto said surface, characterized in that
the application of said preliminary layer comprises (i)

25   immersing said surface in a zinc-containing alkaline
solution, (ii) applying a potential to the sheet to cause

an electrolytic current to flow, and (iii) reversing the
polarity of said potential at least once.

10.   A method according to claim 9 in which the
preliminary layer is applied in an amount of from 0.1 to
0.5 g/m².

11.   A method according to claim 9 or 10 in which said
polarity of said potential is reversed at least twice.

12.   A method according to claim 11 in which the time
interval between each two adjacent polarity reversals is
at least 0.5 s.

13.   A method according to any one of claims 9 to 11 in
which during the application of said potential, said
sheet is initially an anode and is finally a cathode.

14.   A method according to any one of claims 9 to 13 in
which the current density during the application of said
preliminary layer is from 0.5 to 20 A/dm².

15.   A method according to any one of claims 9 to 14 in
which said zinc-containing alkaline solution comprises
from 10 to 300 g/l of NaOH and from 2 to 40 g/l of ZnO.

16.   A method according to any one of claims 9 to 15 in which said pretreating step includes anodizing said surface after applying said preliminary layer.

5   17.   A method according to any one of claims 9 to 16 in which said electrolytic galvanizing is performed with a direct current having a current density of from 10 to 100 A/dm^2, a bath temperature of from 20 to 70°C, a treatment time of from 5 to 90 s, an electrolyte composition

10   comprising zinc sulphate in an amount of zinc from 30 to 200 g/l, and an electrolyte pH of less than 4.

18.   An aluminium or aluminium alloy sheet having an electrolytically applied layer comprising zinc, produced by a method in accordance with any one of claims 1 to 7

15   and 9 to 17.

19.   A building sheet comprising an aluminium or aluminium alloy sheet according to claim 8 or 18 in which

20   the weight of said layer comprising zinc is from 10 to 300 g/m^2.

20.   A building sheet according to claim 19 which is a roofing sheet.

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21. A building sheet according to claim 19 or 20 in which the weight of said layer comprising zinc is from 30 to 100 g/m^2.

5   22. An automotive body sheet comprising an aluminium or aluminium alloy sheet according to claim 8 or 18 in which the weight of said layer comprising zinc is from 5 to 40 g/m^2.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C25D5/44   C25F3/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C25D   C25F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 7709 Derwent Publications Ltd., London, GB; AN 77-15171y XP002021945 & JP 52 005 630 A (SUMITOMO ELEC. IND. KK) , 17 January 1977 see abstract -----	1,8,18

☐ Further documents are listed in the continuation of box C.   ☐ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 July 1997	05.08.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Van Leeuwen, R